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The Role of Degree of Substitution of Cationic Starch on Optimizing Retention

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THE ROLE OF DEGREE OF SUBSTITUTION OF CATIONIC STARCH ON OPTIMIZING RETENTION

BY

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ABSTRACT

The objective of my work was to show experimentally with the use of statistics whether it is more beneficial to optimize the degree of substitution of a cationic starch rather than the addition rate to maximize retention.

Fines retention, as measured using the Dynamic Retention/Drainage Jar (Britt Jar), served as the method of experimental evaluation. Three starches were studied ranging in degree of substitution from 0.014 to 0.0833 at a constant molecular weight. Calcium carbonate was used as the filler fraction because it can be quantitatively analyzed via an EDTA titration. Starch furnish used was four, eight, and twelve pounds per ton along with a 30% filler level. Colloid Titrations were used in determining the ionic demand of the system.

As shown by multiple regression analysis of the data, it is equally beneficial to either optimize the degree of substitution or the amount added to maximize retention. In addition, the Colloid Titration Ratio was not a good predictor of the ionic demand of the system.

INTRODUCTION

The subject of this thesis is to determine if there is any difference in retention achieved from varying the degree of substitution rather than the addition rate of a high molecular weight cationic starch. In the following review many topics are discussed including the definition of fines and fines retention and the factors effecting retention. In addition, the mechanisms of flocculation as they pertain to retention will be considered.

ANALYSIS OF LITERATURE

BACKGROUND

When dealing with wet end chemistry it is common to talk about dispersed solids in water. The particles in this system are usually defined in terms of their size alone, which are: gross dispersion, colloidal dispersion, and ionic dispersion. (1) For optimum results in retention it is necessary to control the electrokinetics of the papermaking system. The main mechanism of controlling the fines loss is by flocculation.

FINES

The definition used for this experiment for fines is suggested by Britt: (2) fines are all cellulosic and mineral material passing through a 200 mesh (75 μm diameter hole) screen. Retention of these fines is important for several reasons: (3)

1. Recovery of material costs.
2. Improvement of paper properties.

3. Reduction of BOD.
4. Reduction of fiber depositing.
5. Increased drainage rate due to reduction in hydrodynamic surface area brought by fines and filler area.

However, Britt states that maximum retention is not always a good papermaking practice. (2) There are many unwanted effects from increased retention such as drainage problems, poor formation, and inefficient utilization of pigment. (3)

MECHANISM OF FLOCCULATION

It is generally accepted that particle aggregation can occur via three basic mechanisms. These are:

1. Charge neutralization.
2. Electrostatic patch formation.
3. Bridging.

CHARGE NEUTRALIZATION

This can be defined as coagulation because it accomplishes the reduction of interparticle repulsion and can be produced by the following methods: (6)

1. Introduction of an ion of opposite charge which is specifically adsorbed.
2. Change in pH.
3. Compression of the diffuse layer by increasing the concentration of the counterions.

Rapid coagulation occurs on or around the isoelectric point and any further addition of electrolyte beyond that required for this point does not increase coagulation.

ELECTROSTATIC PATCH FORMATION

The electrostatic patch model involves partial neutralization of the surface charge of the particles. (7) The result of flocculation is caused by the attraction between the positive and negative charge sites on the particles.

BRIDGING THEORY

FLOCCULATION TYPE

Flocculation is considered a special case of coagulation. The bridging action of polymers forms a loose, three dimensional floc. Britt and Unbehend suggest that the only difference between coagulation retention aids and flocculation aids is that the latter have a molecular weight that allows one molecule to be attached simultaneously to several particles. (9)

Two basic types of flocs have been proposed. (10,11,12) One type is called a "hard floc" which resists redispersion by shearing action. The other is called a "soft floc" and is easily dispersed by shearing action. Molecular weight seems to play an important role in resistance of flocs to shear. (13,19) The higher the molecular weight, the more shear resistant the flocs that are formed. (6,9)

ADSORPTION

Bridging is accomplished basically by segments of a polymer molecule adsorbing onto the surface of a particle and the other segments of the molecule adsorbing onto uncovered surfaces of a second particle. [8,14] Strazdins suggested that the long polymer chains gather the fines by the bridging mechanism and deliver them to the fibers. [14]

Adsorption of the polymer chain onto the surface is dependent on the shear conditions at the interface. [8] The configuration of the polymer adsorbed onto the surface is determined by the charge density of the polymer. [8,15,16,17] Flatter configurations are assumed by polymers of higher charge densities due to the larger interaction energies with the surface. [6]

According to Arvela, Swanson, and Stratton, molecular weight has a secondary effect on adsorption. [18] they suggested that the dependence on molecular weight is a function of the charge of the molecule and is usually negligible.

OPTIMUM POLYMER CONCENTRATION

LaMer and Healy have found that there is an optimum polymer concentration for flocculation that is governed by two competing processes. [8] As the polymer concentration increases there is more polymer to react, however, as this reaction takes place more and

more available reaction sites are taken up thus decreasing the effectiveness of adding so much polymer to begin with. Optimum polymer concentration has been found to be independent of molecular weight but dependent upon agitation time and agitation intensity. (15)

The requirements for flocculation by bridging are as follows: (6)

1. Extended segments must be available for bridging.
2. These segments must be sufficient length and number to form stable flocs by bridging.
3. Free surface area must be available to act as bridge sites.

A flocculated system can become or remain dispersed if any of the following occurs: (6)

1. The surface of the particles become so saturated that bridging cannot occur.
2. The extended segments physically interfere with one another and prevent bridge formation.

MOLECULAR WEIGHT

Longer chains will result in longer more numerous loops available for bridging. (6) Yorke found that the optimum molecular weight depends on the size of the particles to be flocculated. (19)

According to Dobbins, the ideal system would be to floc the fines/filler portion to improve retention and not to floc the long

fibers in the system to preserve formation and the final physical and optical properties of the sheet. (4) However, this system cannot be obtained as noted by the author. The order of adsorption of particles by the cationic polymers are those with high surface area, high charge density first, and those with decreasing surface area and charge density in succession. Hence, there is no selective adsorption and the long fibers flocculate along with the fines. The optimum amount of flocculation, controlled by polymer addition, lies somewhere near the point where the retention of fines has been maximized, but where the flocculation of long fibers has not yet begun. (3)

FACTORS EFFECTING FLOCCULATION

King and Williams point out that polymer bridging must be able to withstand shear forces to remain effective. (5) Other factors which influence the effectiveness of floc formation and stability include polymer type, polymer concentration, electrolyte type, electrolyte concentration, fines addition level, agitation level, and pH. (3) Studies have shown that a high molecular weight, low charge density polymer under minimal shear will give the best retention.

The characteristics of the pulp furnish used can effect retention. The average fiber length, fiber length distribution, fiber flexibility, fiber surface roughness have been found to effect retention by affecting fiber/fines flocculation. (23) In addition, due to more surface area generated by refining, furnishes that are refined more retain more fines.

The machine variables used during the papermaking process directly affect retention. Due to the mechanical retention, reducing machine speed, reducing the vacuum in the suction boxes, and using hydrafoils instead of table rolls all increase retention. (6) Also, machine speed increase reduces retention due to more shear generated which degrades the flocs that were formed.

The soluble fraction of a furnish also effect retention. Again as seen in Table 1, there are a variety of soluble species which contribute to the cationic demand of the system. Another factor affecting retention is the protective colloid effect. This occurs when: (6)

1. The surface of the colloid is partially soluble, forming a gel like structure.
2. When various white water components absorb onto the surface of the particles.

ELECTROKINETICS

The repulsive forces that are present in papermaking systems and that prevent flocculation without the addition of chemicals are of an electrical nature. (6) The charge on the surface of the fines is responsible for the repulsion since like charges repel one another. The surface charges occur due to: (20)

1. Ionization of molecules on the surface, or
2. Selective adsorption of specific ions from solution, or
3. Faults or defects in the crystal lattice, or

4. Partial solution of a crystal lattice.

The zeta potential is an indication of the repulsion of the suspended particles in the papermaking system. The zeta potential is defined in Figure 1. It is reflection of a system of adsorbed ions and counterions. In terms of paper fiber, which inherently carries a negative charge, opposite charged ions are attracted to and near the surface of the solid. The next layer, known as the Stern Layer, contains immobilized counterions. The Gouy Layer, which is adjacent to the Stern Layer is made up of the rest of the counter ions. There is a definite thickness of surrounding liquid bound to the particle. The electrical potential at the plane of shear between the bound liquid and the free liquid is the zeta potential.

As seen in Table 1, there are many soluble and fiber/fines associated charged species all of which contribute to the zeta potential of a system. When the zeta potential has been neutralized, the iso electric point of the particle has been reached which makes them susceptible to flocculation. Hence, due to low repulsion of particles in the system high retention is favored. Valette proposed that the zeta potential, and thus the repulsive energy potential is sensitive to both the nature of the water and the pH of the solution. (21) In addition, fiber type, filler type, alum dose, polymer addition and wet end additives also have an effect on zeta potential. Arno, Frankle, and Sheridan proposed that the zeta potential of a furnish is a composite of the zeta potentials of all the particle types in the system; each particle type has a unique zeta potential dependent on the shape of the particle. (22)

Table 1

Soluble and Fiber/Fines Associated Charged Species

Substance	Effect on Wet End Chemistry	Contribution to Charge determination
sodium	very slight	none
calcium	moderate at high conc.	slight
magnesium	moderate at high conc.	slight
alumina	large	moderate
acid pH	large	small
sulfate	moderate at high conc.	none
chloride	none	none
lignin	large	large
tannins	large	large
dispersants	large	large
coagulants	large	large
cellulose	large	large a
filler	large	large a

a = These effects are seen in determination on total cationic demand.

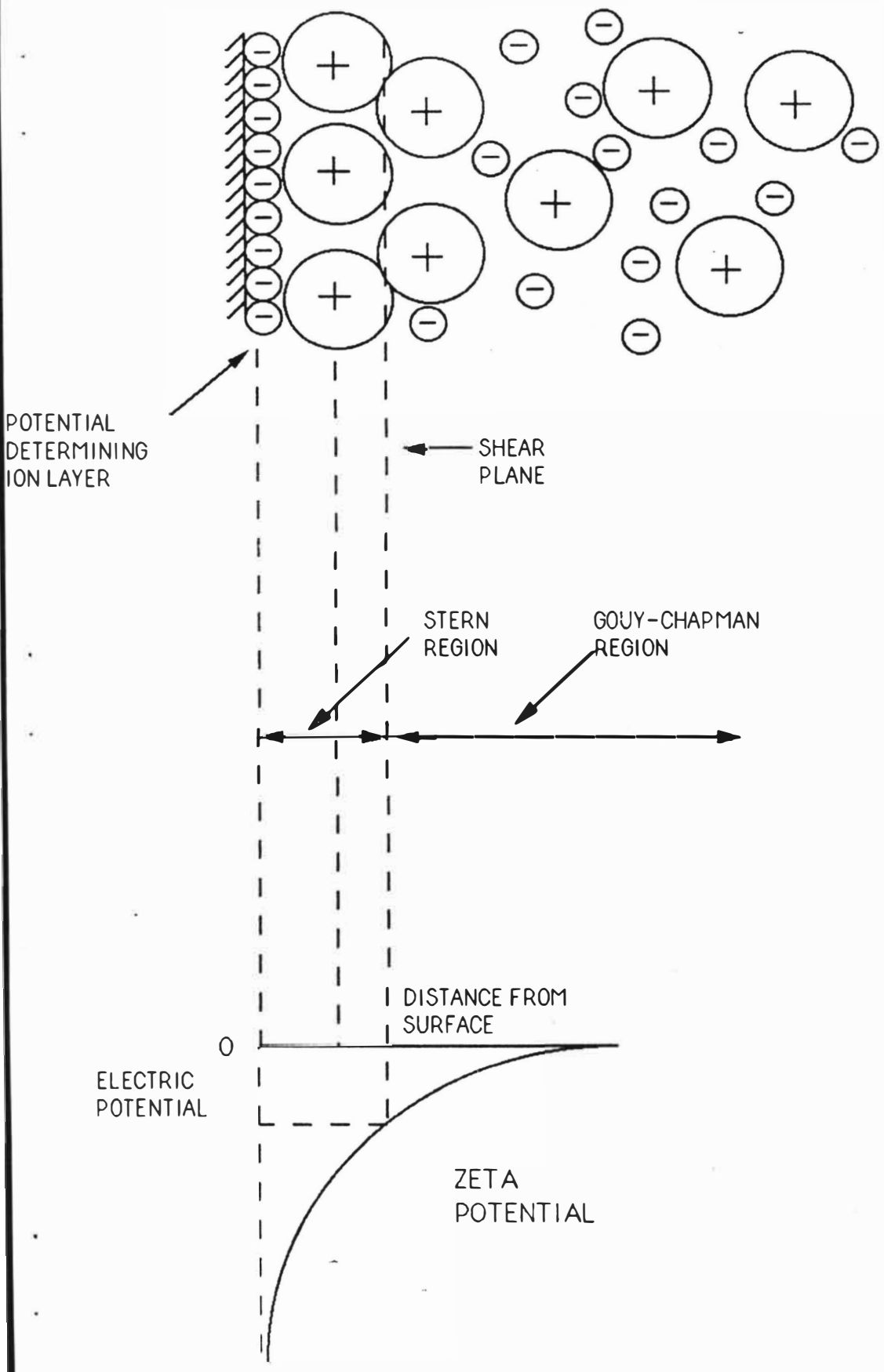


FIGURE 1 - ZETA POTENTIAL SCHEME

CHARGE AND WET END CHEMISTRY

Papermaking furnishes contain many charged materials which all have a profound influence on the retention of fine solids and chemical additives. The Charge Determination technique can be used as a powerful diagnostic tool since it measures the sign and magnitude of the charge. Charge Determination measures directly the combined total of soluble charge and particle charge. As shown in Table 1, not all soluble and fiber/fine charged species are detected in Charge Determination nor are all of them a factor in wet end chemistry as noted in the Table.

CHARGE DETERMINATION

The water from papermaking furnishes can be titrated much like an acid base titration to an end point of zero charge. This is what is called Charge Determination. The value and sign of the charge depends on the quantity of titrants used to reach the end point. This quantitative charge is useful in diagnosing retention studies.

The Charge Determination method measures directly the water soluble charge only of the furnish. By appropriate experimentation the charge demand of the entire furnish can be determined by taking each fraction separately and measuring its charge. However, it is important to note the Charge Determination value is not identical to zeta potential. Charge Determination measures the amount of cationic flocculant needed to satisfy the actual and potential anionic charge of the water/fiber system. The suspended solids in a furnish can continue to adsorb the cationic polymer past the point of zero zeta potential. This is a function of the ion exchange

capacity of the pulp and filler. Polymers can adsorb against electrical charge barriers even onto neutral surfaces.

The total amount of cationic polymer that a furnish will adsorb is the sum of the following charge demands:

1. Soluble anionic charge.
2. Actual anionic charge on the surfaces of fiber and fines.
3. Ion exchange potential of fiber and fines.

Charge Determination measures directly only the first. The sum of 2. and 3. is determined indirectly through a series of titrations described in the experimental plan.

CATIONIC STARCHES

The basic repeating unit of starch is an anhydroglucose unit. These units polymerize through alpha (1,4) or alpha (1,6) linkages to form amylose or amylopectin respectively. A common starch consists of both polymers and some respective percentages are seen in Table 2.

Table 2.

Amylose and Amylopectin Content of Various Starches

Starch type	% Amylopectin	% Amylose
Regular Corn	73	27
Potato	80	20
Waxy Maize	100	0
High Amylose	20	80

Variations in the ratio of amylose to amylopectin will result in variations in viscosity, molecular weight, and charge distribution. (24)

Cationic starches can be prepared by a variety of methods with three of these being:

1. Reaction of starch with beta-halogenated amines in the presence of NaOH.
2. Reaction of starch glycidyl tertiary amines in the presence of NaOH.
3. Reaction of starch with epoxypropyltrimethyl-ammonium chloride.

The third method prepares a quartenary amine starch which could be represented by the following formula.

$$Starch\text{-}R\text{-}O\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}N^{+}\text{-}(CH_3)_3 \ + Cl^{-}$$

Cationic starches prepared using primary, secondary, or tertiary amines must be used in acid systems to attain positive charge. "Onium starches" are starch derivatives bearing fully substituted radicals such as quartenary amines, quartenary phosphates, or tertiary sulfonates. These starches carry a full positive charge over the entire pH range.

Unmodified starches are not retained well in the sheet and the retention that does occur is reversible; over 80% of the starch adsorbed by paper can be removed by heating the paper in water. (25) Cationic starches are strongly adsorbed by fibers and this retention is irreversible; 85% of the adsorbed starch remains when the paper is placed in boiling water and can be redissolved only by washing

with strong acid. [25] As such, cationic starches will remain adsorbed to the fibers during processing and reuse of paper mill broke, will not contribute to the BOD of the mill effluent as unmodified starches do. [25] J. Marton and T.Marton [25]have studied cationic starch adsorption by cellulose fibers and reported the following:

1. Cellulose fines retain more cationic starch than do fibers.
2. Increased refining increases the adsorption of the cationic starch.
3. Softwood and hardwood fibers retain cationic starch equally well.
4. Dried pulps retain less cationic starch than never dried pulps.
5. The adsorbing capacity of fibers increases as carboxyl content increases.
6. Alumina precipitated on a fiber reduces its adsorptivity of cationic starch.

CONCLUSION

The use of cationic starch as a retention aid has been used successfully in many mill applications. Reduced rosin consumption, the use of cheaper filler with no appreciable loss in strength or printing performance, and increased machine speeds due to increased drainage rate allowed production cost at one mill to be reduced when cationic starch was used as a retention aid. [27] Van der Burgh found that the other effects os using wet end cationic starch included:[28]

1. Reduced picking at the press rolls.

2. Faster machine equilibration after grade changes due to improved one pass retention.
3. Better color retention due to increased retention of pigmented dyes and the fines to which these dyes are adsorbed.
4. Less sheet two sidedness due to more uniform retention throughout the sheet.
5. Less paper shrinkage during drying.
6. Change in sheet porosity.

STATEMENT OF PROBLEM

A discussion of the complexity of fines with relation to their retention has been included in the previous literature search. It is the intention of this study to experimentally show the effects of degree of substitution at constant molecular weight and through the use of statistics develop a model for prediction of the optimum degree of substitution.

The primary purpose of this work is to show if it is more beneficial to optimize the degree of substitution rather than the addition rate to maximize retention of fines. This comparison will be done by using mathematical models generated by regression analysis. The dependent variable in the model will be retention values(First Pass, Total Fines, and $CaCO_3$), and the independent variables will be the addition rate and the degree of substitution. The Colloid Titration Ratio test will be used to determine the cationic demand of each system and the DRJ will be used to determine the retention achieved by each chemical system.

The relationship between degree of substitution of cationic polymers and fines retention has been studied previously. However, no work has to the author's knowledge been done to see if it is beneficial to optimize the degree of substitution per system rather than the addition rate. Therefore the results of this research could prove beneficial in the approach that papermills take in selection of a cationic starch that is to be used as a retention aid.

OBJECTIVES

1. To experimentally establish a relationship between the degree of substitution of a cationic starch and its fines retention capability.
2. To develop statistical models via regression analysis of results to show effects of degree of substitution and addition rate.
3. To show if it is better to optimize the degree of substitution rather than the addition rate to maximize retention of fines.

EXPERIMENTAL

TESTING METHODS

The overall experimental approach is to use a Dynamic Retention/Drainage Jar (DRJ), a Colloidal Titration and a hardness titration to generate results for comparison of various starches in

determining which variable affects retention the most.

The DRJ, developed by Britt and Unbehend measures the effect of turbulence on colloidal retention (retention due to van der Waals and electrostatic forces) independent of the mechanical variables that effect retention.[9] Isolation and elimination of the effect of mechanical factors in the DRJ is accomplished:

1. Preventing mat formation.
2. Controlling screen mesh size by using electrodeposited screens having precisely controlled hole size.
3. Using an agitator speed system to control turbulence.

The DRJ attempts to simulate the headbox slice and the wire section that immediately follows where there is little retention due to entrapment in the fiber mat as the mat is in dynamic state. A large fraction of the unretained fines are lost to the white water at the slice and in the initial forming area. Thus, the DRJ is a useful method to examine retention of a papermachine in the laboratory. Data from the DRJ can be correlated to an actual papermachine by determining the turbulence level in the jar that matches that on the machine. This is accomplished by matching the one pass retention level of the machine with the turbulence in the jar that gives the same retention level using a "flocculation index" curve.[9]

In carrying out the experimentation necessary to accomplish the objectives, the following was used:

Fiber

-80% Bleached Hardwood Kraft

-20% Bleached Softwood Kraft

Filler

-30% $CaCO_3$

The fiber fraction was refined at 1.57% consistency in the laboratory Valley beater to approximately 400 ml. CSF. An appropriate amount of filler was added to achieve the 30% target. The resultant furnish was then diluted to 0.50%.

MATERIALS

The starches to be used were experimentally developed by a starch manufacturing company using amylopectin as the parent molecule. The starches had been precipitated from the paste form in which they were converted using methanol. The degree of substitution data, obtained from the Kjeldahl procedure for nitrogen determination, was provided by the starch supplier.
The following starches were used.

Molecular Weight	High
Degree of Substitution	.0226
	.0307
	.0833

The starches were cooked at 20.0% solids and then diluted to 0.50% for application.

FINES RETENTION PROCEDURE

Three various degrees of substitution along with three various addition rates and corresponding blank runs were studied. These runs were done in triplicate to yield a total of thirty different experiments. A random number generator was used to designate the order the experiments. This was done to eliminate any systematic errors that could have occurred in the experiment.

The DRJ was used to determine the retention characteristics of the system. A 200 mesh (75 μm) screen was used along with a vaned drainage chamber (see Figure 2). The fiber furnish consisted of a blend of 80% bleached hardwood kraft and 20% bleached softwood kraft along with 30% $CaCO_3$ based on dry fiber. The fibers were then refined to 400 ml CSF using a laboratory Valley beater, filler was then added, and the resultant pulp the diluted to 0.50% consistency. The procedure was as follows.

1. Measure out 500 ml.
2. Pour into DRJ and agitate at 400 RPM
3. Add starch - mix for 1 min.
4. Turn up RPM to 750 - mix for 1 min.
5. Collect sample in pre-tared 4 oz. plastic bottle w/lid
6. Take excess of 50 ml. of Hbox stock for Colloid Titration
7. Weigh sample bottle.
8. Add 5 ml. of 5N HCl
9. Wait 1/2 hour
10. Filter fiber on tared filter paper and collect filtrate
11. Measure out with pipette 25.0 ml. aliquot and place in 100 ml. beaker. Add 1 - 2 ml. of hardness buffer and enough indicator for medium pink color.
12. Titrate with .02N EDTA to blue end point. Record Titer
13. Take 500 ml. of Hbox* furnish and repeat steps 7-12
14. Measure out 100 ml. samples for fines analysis. Pour sample into DRJ. Dilute to 500 ml., and turn on agitator to 1000 RPM. Add 5 ml. of Tamol and let mix. Drain, rinse and repeat several times. Rinse off

fiber from screen onto tared filter paper. Dry and weigh.

$$\% \text{ fines} = \frac{[(\text{Hbox cons.}) - (\text{wt. of fiber})]100}{(\text{Hbox cons.})}$$

15. Take process water samples for Hardness Titration.

COLLOID TITRATION RATIO

To determine the colloid titration ratio a 50 ml. sample of as is stock is diluted to 500 ml. Then four 100 ml. aliquots are then taken and pour into 250 ml. beakers. A magnetic stir bar is then used and the test is then run according to Fig. 3. It should be noted that after the addition of 10 mls. of either polymer the solution was allowed to mix for one minute. DDPM is the cationic polymer and PVSAK is the anionic polymer and both are 0.1N.

RETENTION CALCULATIONS

To determine the percent $CaCO_3$ retention, a Hardness Titration was done.

*Hbox is an abbreviation for Headbox.

A 25.0 ml. aliquot was transferred via a pipette to a 100 ml. beaker. 5 ml. of 5N HCl was added to dissolve the $CaCO_3$ via the following reaction:

$$CaCO_3 + 2\,HCl = CaCl_2 + H_2CO_3 \text{ (soluble salt)}$$

1 - 2 mls. of hardness buffer was added along with

Eriochrome Black T indicator to give a medium pink color. A blank was run on the process water used in actual $CaCO_3$ retention. The percent $CaCO_3$ retention was calculated as follows.

$$\text{wt. } CaCO_3 = \frac{\text{(ml EDTA smpl. - ml EDTA blank)}}{\text{10 (ml of sample)}}$$

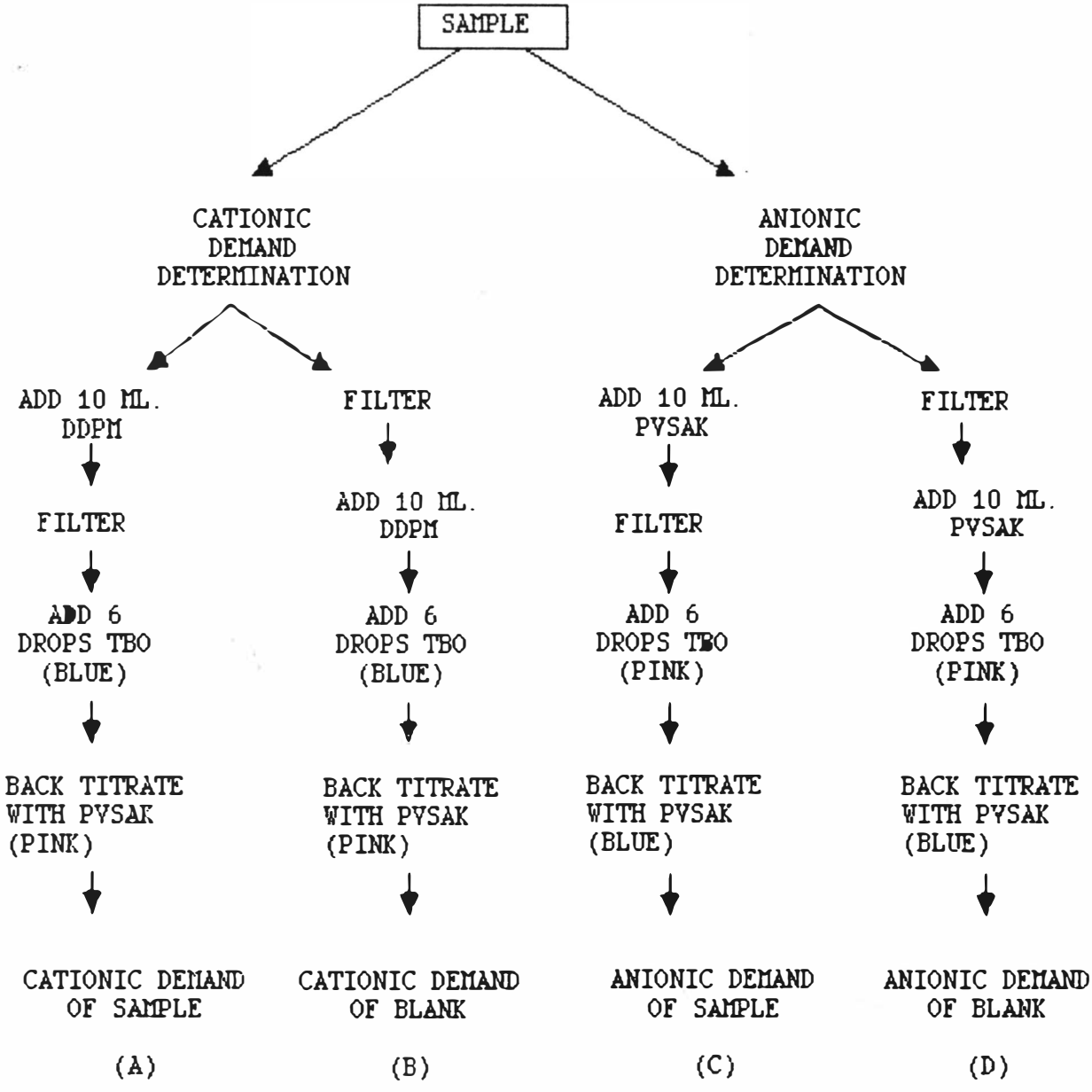
$$\%\ CaCO_3 \text{ retained} = \frac{\text{(wt. } CaCO_3 \text{ Hbox - wt. } CaCO_3 \text{ smpl.)100}}{\text{wt. CaCO3 Hbox}}$$

$$\%\ \text{First Pass} = \frac{\text{(wt. Hbox - wt. smpl.)100}}{\text{wt. Hbox}}$$

$$\%\ \text{Total fines}^{*} = \frac{\text{(.38(wt. Hbox) - wt. smpl.)100}}{\text{.38(wt. Hbox)}}$$

*.38 IS FROM TOTAL FINES CALCULATED BY BRITT DEFINITION.

FIGURE 2 - COLLOID TITRATION RATIO



(B-A) = CATIONIC DEMAND OF STOCK

(D-C) = ANIONIC DEMAND OF STOCK

$$\frac{(D-C)}{(B-A)} = \text{COLLOID TITRATION RATIO}$$

PRESENTATION AND DISCUSSION OF RESULTS

The results of these experiments will be evaluated and presented on the basis of calcium carbonate, total fines and first pass retention. The retention is relative to degree of substitution and addition rate. The results will be discussed as they relate to one another in a statistical model.

STATISTICAL ANALYSES

It was the intention of this study to analyze the data with the use of regression analysis and analysis of variance. The objective of regression analysis is to find a model which is both simple (relatively few parameters) and provides a good fit to the data. The first step taken in regression analysis is to find out which model actually fits the relationship between the dependent and independent variable. In this experiment there were two independent variables (degree of substitution and addition rate) and one dependent variable (retention values). Therefore, plots of retention versus addition rate and retention versus degree of substitution were generated. The purpose of this was to see what type of mathematical relationship existed. Figures 3 - 8 show that a quadratic provide the best fit to the data.Each point on the plots is the mean of three determination of retention. The error bars shown represent one standard deviation above and below the mean of three determinations. Hence, a quadratic regression model was used for comparison purposes.

FIGURE 2 - PROOF FOR QUADRATIC REGRESSION MODEL FOR TOTAL FINES RETENTION

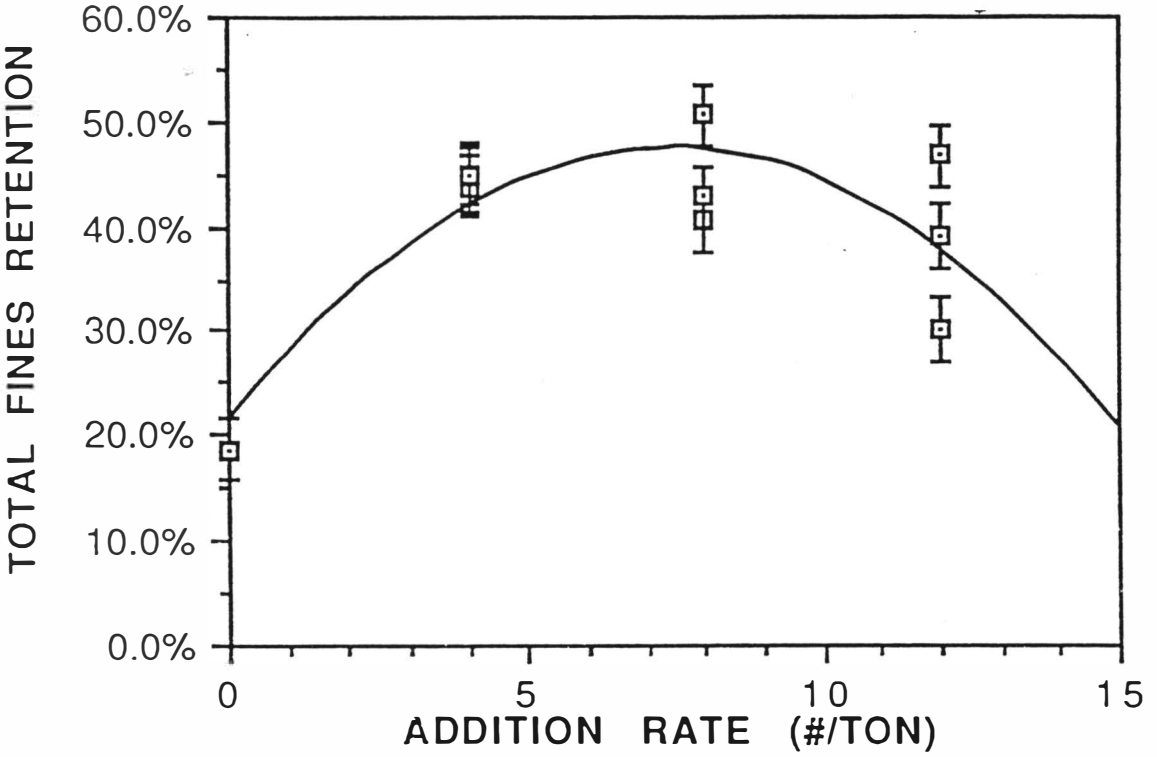


FIGURE 3 - PROOF FOR QUADRATIC REGRESSION MODEL FOR TOTAL FINES RETENTION

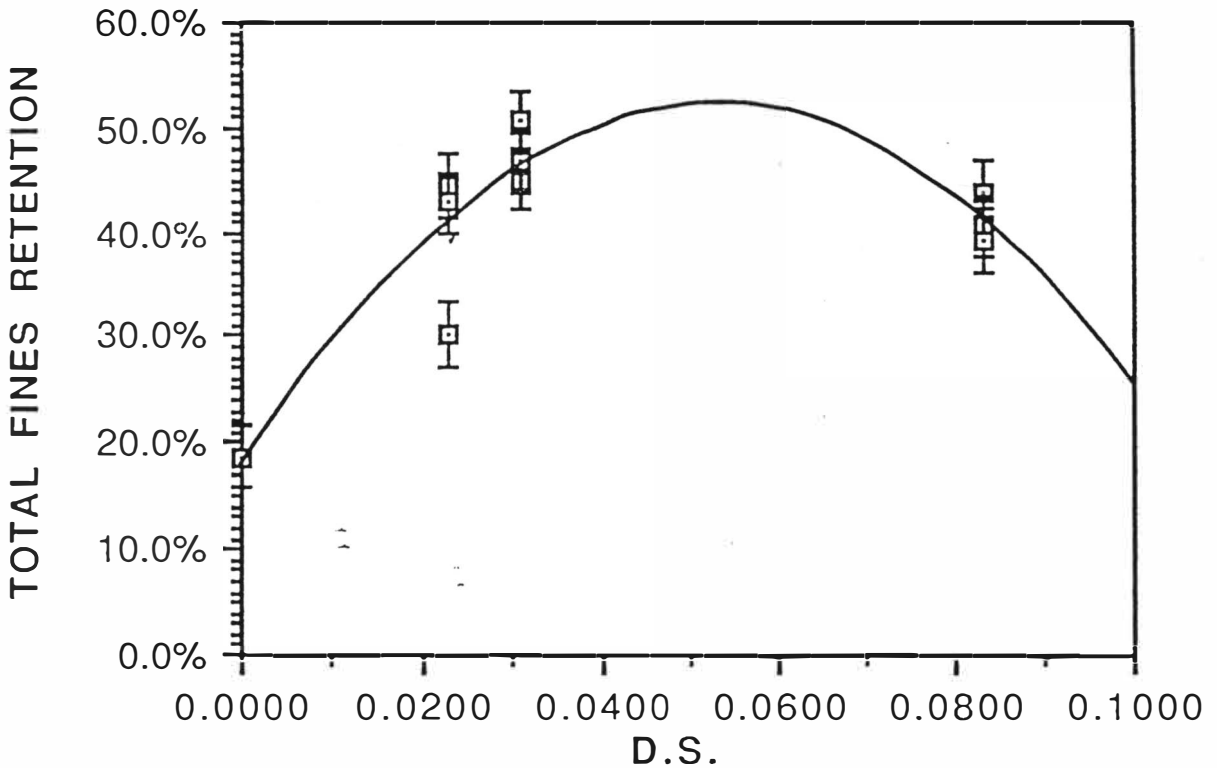


FIGURE 4 - PROOF FOR QUADRATIC REGRESSION MODEL FOR FIRST PASS RETENTION

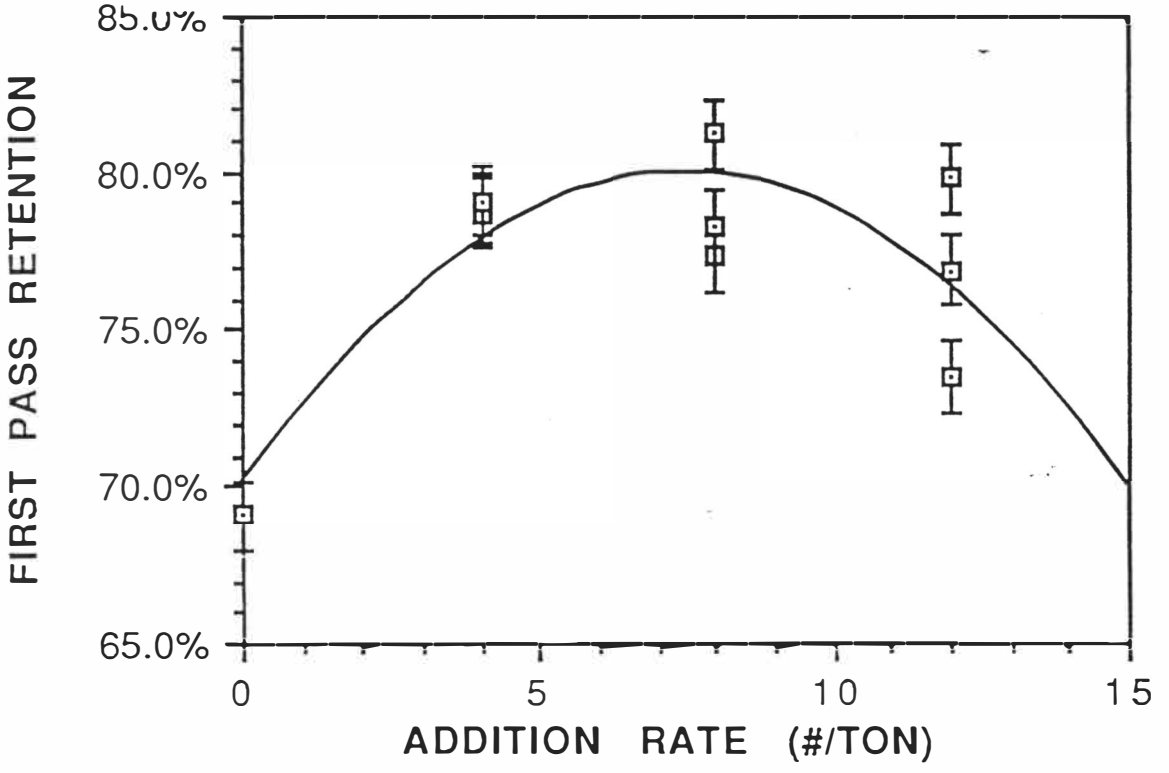


FIGURE 5 - PROOF FOR QUADRATIC REGRESSION MODEL FOR FIRST PASS RETENTION

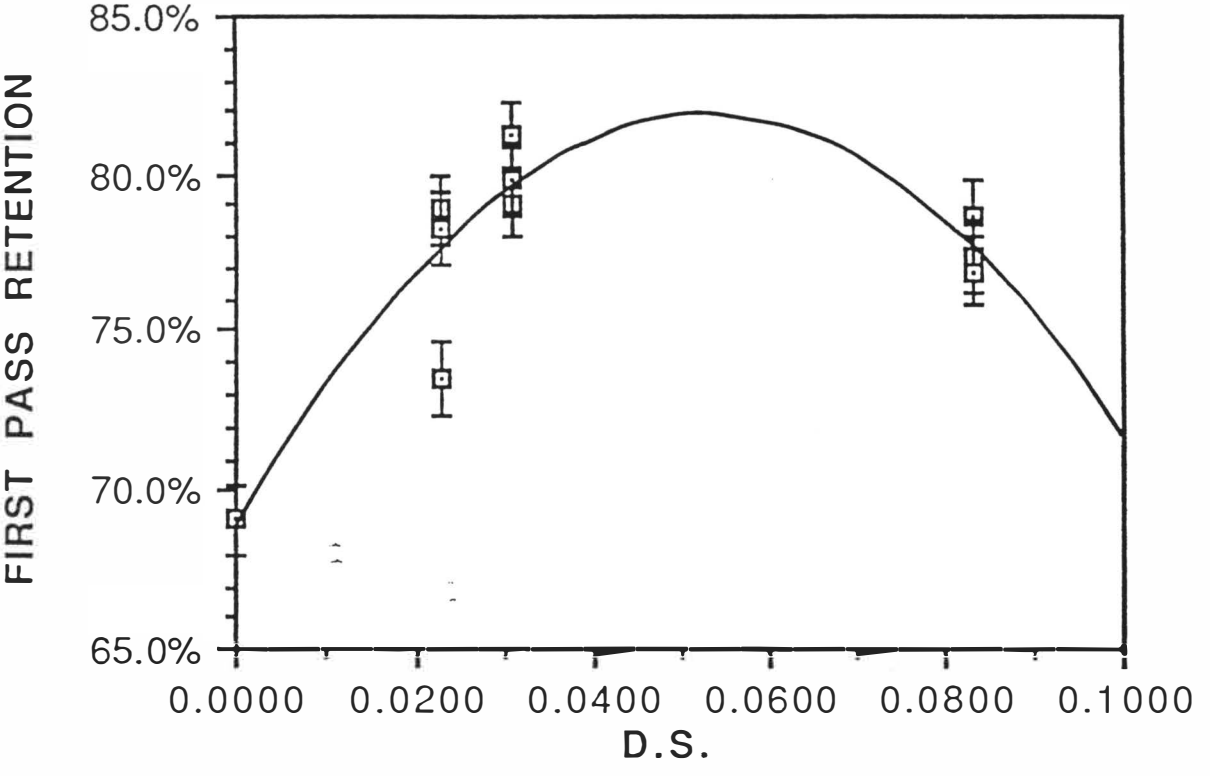


FIGURE 6 - PROOF FOR QUADRATIC REGRESSION MODEL FOR CALCIUM CARBONATE RETENTION

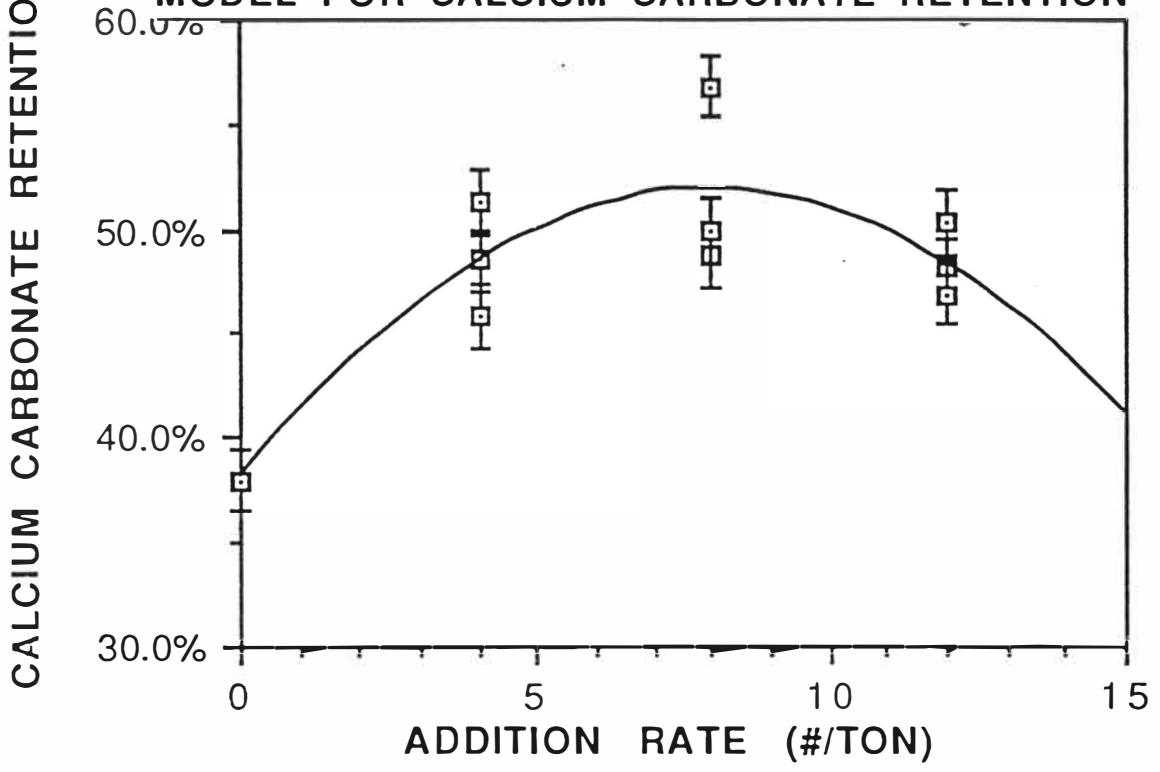
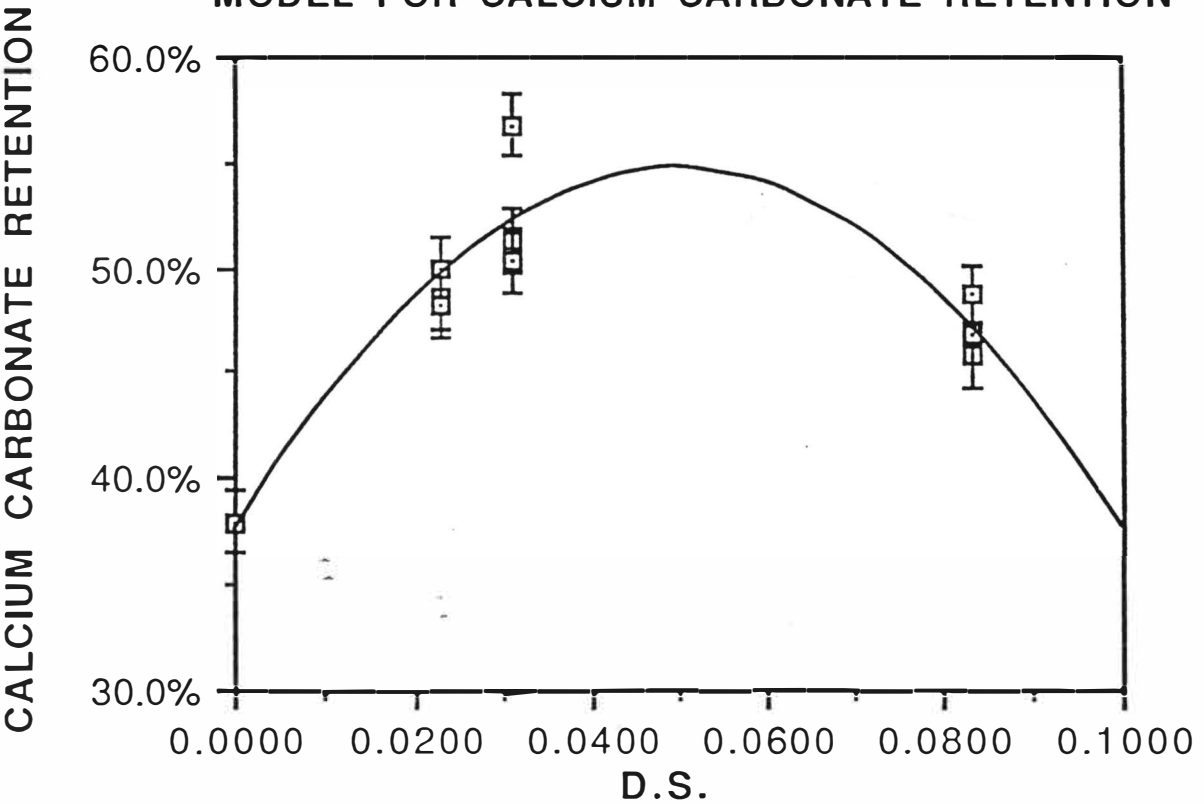


FIGURE 7 - PROOF FOR QUADRATIC REGRESSION MODEL FOR CALCIUM CARBONATE RETENTION



There are several statistical tests that can be used to test the utility of the model that was generated through regression analysis. These tests are all a part of analysis of variance. The tests used were the t-ratio, the F test and the p test.

The t-ratio is a test to see if the constant, linear, and quadratic terms were necessary in the regression model.

$$H_0 : \beta_2 = 0, \quad H_a : \beta_2 \neq 0$$

H_0 here says that the term is not necessary. Hence, for the model to be used H_0 must be rejected. For 95% confidence H_0 is rejected if $t_{.05,7} \geq 2.179$ or $t_{.05,7} \leq -2.179$. As seen in Table 4 each individual regression term for every model is necessary to describe the relationship that existed.

The F test is used to verify if the quadratic regression model explains most of the variation in he observed values. The F value is actually the ratio of explained variation to unexplained variation. The null hypothesis for this test is as follows:

$$H_0 : \beta_1 = \beta_2 = 0, \quad H_a : @ \text{ least one } \beta \neq 0$$

For a 95% confidence $F_{.05,2,7}$ must be > 4.74. If the explained variation is high relative to unexplained, H_0 would naturally be rejected and this would confirm the utility of the model. As seen in Tables 5 - 7, the F values for each individual model were greater than 4.74.

TABLE 4 - t-ratio TEST FOR QUADRATIC REGRESSION

FIRST PASS RETENTION

x = #/TON

PREDICTOR	t - ratio
constant	33.56
x	3.87
x^2	-3.63

x = degree of substitution

PREDICTOR	t - ratio
constant	38.61
x	5.04
x^2	-4.75

CALCIUM CARBONATE RETENTION

x = #/TON

PREDICTOR	t - ratio
constant	14.14
x	3.92
x^2	-3.43

x = degree of substitution

PREDICTOR	t - ratio
constant	17.77
x	5.91
x^2	-5.92

TOTAL FINES RETENTION

x = #/TON

PREDICTOR	t - ratio
constant	3.88
x	3.87
x^2	-3.63

x = degree of substitution

PREDICTOR	t - ratio
constant	3.76
x	5.00
x^2	-4.72

TABLE 5 - FIRST PASS REGRESSION ANALYSIS AND ANOVA

y = .701 +.0265 x-.00177x^2

dy/dx = 0 leads to x = 7.5 #/TON

y(f) = 80.0 ± 5.6 %

s = .02248 s(f) = .00998

y = RETENTION
x = #/TON
R^2 = 68.4%
F = 7.58
p = .02

y = .687 + 4.93 x- 46.2 x^2

dy/dx = 0 leads to x = .0534

y(f) = 81.9 ± 4.6 %

s = .01837 s(f) = .00826

y = RETENTION
x = D.S.
R^2 = 78.9%
F = 13.1
p = .00

TABLE 6 - $CaCO_3$ REGRESSION ANALYSIS AND ANOVA

$y = .381 + .0346x - .00217x^2$

$dy/dx = 0$ leads to $x = 8.0$ #/TON

$y(f) = 51.9 \pm 3.2$ %

$s = .02889$ $s(f) = .01287$

y = RETENTION
x = #/TON
$R^2 = 70.8\%$
F = 8.5
p = .01

$y = .376 + 6.86x - 68.4x^2$

$dy/dx = 0$ leads to $x = .0501$

$y(f) = 54.8 \pm 2.4$ %

$s = .02182$ $s(f) = .00981$

y = RETENTION
x = D.S.
$R^2 = 78.9\%$
F = 13.1
p = .00

TABLE 7- TOTAL FINES REGRESSION ANALYSIS AND ANOVA

y = .213 +.0699 x-.00468 x^2

dy/dx = 0 leads to x = 7.5 #/TON

y(f) = 47.4 ± 6.5%

s = .05924 s(f) = .0263

y = RETENTION
x = #/TON
R^2 = 68.4%
F = 7.58
p = .02

y = .178 + 13.0 x -122.0 x^2

dy/dx = 0 leads to x = .0533

y(f) = 52.4 ± 5.3 %

s = .04780 s(f) = .0219

y = RETENTION
x = D.S.
R^2 = 78.7%
F = 12.90
p = .00

Another test that was used to test the utility of the model was the p test. The null hypothesis for this test is as follows:

$H_0 : \beta_2 = 0, \quad H_a : \beta_2 \neq 0$

If H_0 is rejected this shows that the complete model is a very useful tool for prediction. For 95% confidence H_0 is rejected if p < .05. Tables 5 - 7 show that all p values are below .05.

The coefficient of multiple determination (R^2) is another number generated through the analysis of variance. This number indicates what percentage of observed variation can actually be explained by the quadratic regression model. For example, as seen in Table 5 R^2 is 68.4%, so this states that 68.4% of the observed variation were explained by the regression equation.

As seen in Table 8 the quality of results indicated by most of the standard deviations are very good. However, some standard deviations were high which led to the insignificant levels for the coefficient of multiple determination.

To compute the maximum values that could be obtained from the basis of the experimental results the first derivative of the regression equation was taken and set equal to zero and solved for x(degree of substitution or addition rate). This led to the maximum value of y (the particular retention being investigated). For comparison of maximum predicted retention values for each situation, 95% confidence interval were generated using the standard deviations of the observed

TABLE 8 - SUMMARY OF RETENTION RESULTS

(#/TON)/D.S.	AVERAGE FIRST PASS	AVERAGE CALCIUM CARBONATE	AVERAGE TOTAL FINES
BLANK	69.1% ±.2	38.0% ±.7	18.7% ±.7
4/.0226	78.9% ±.6	48.5% ±.8	44.5% ±1.6
4/.0307	79.1% ±.3	51.3% ±.7	45.0% ±.9
4/.0833	78.7% ±.1	45.9% ±.6	43.9% ±.2
8/.0226	78.3% ±.2	49.9% ±.3	42.9% ±.5
8/.0307	81.2% ±.2	56.8% ±6	50.6% ±.4
8/.0833	77.4% ±.6	48.7% ±1.1	40.5% ±1.4
12/.0226	73.5% ±.4	48.1% ±.3	30.2% ±1.2
12/.0307	79.8% ±0	50.3% ±0	46.8% ±0
12/.0833	76.9% ±.9	46.9% ±.7	39.1% ±2.3

NUMBERS BELOW THE PERCENTAGES ARE ± ONE STANDARD DEVIATION

and predicted future value. The equation for the confidence interval is as follows:

$$y(f) \pm t_{.025,9}(\sqrt{s^2 + s(f)^2})$$

The results can be seen in Tables 5 - 7.

COLLOID TITRATION RATIO

As shown in Table 9 no trend existed as to what actually happened to the wet end chemistry for each system. The standard deviations were much too great which makes the numbers generated insignificant. A possible explanation could be that not all titrations were done on the same day. Also, since the color change is observed by eye, human error could be high. Hence, this is not a very good research tool to be used unless an instrument can be used to indicate color change.

TABLE 9 - SUMMARY OF COLLOID TITRATION

($/TON)/D.S.	AVERAGE ANIONIC DEMAND	AVERAGE CATIONIC DEMAND	AVERAGE CTR
BLANK	0.13 ±0.06	2.57 ±0.21	0.05 ±0.02
4/.014	0.63 ±0.49	2.10 ±0.35	0.32 ±0.27
4/.0307	0.47 ±0.15	1.77 ±0.57	0.27 ±0.09
4/.0833	1.50 ±0.78	1.03 ±1.01	3.02 ±2.46
8/.014	0.77 ±0.31	1.77 ±0.21	0.44 ±0.19
8/.0307	0.90 ±0.75	2.67 ±1.33	0.31 ±0.19
8/.0833	0.90 ±0.46	1.57 ±0.21	0.56 ±0.21
12/.014	0.70 ±0	1.53 ±0.83	0.63 ±0.47
12/.0307	1.10 ±0.26	2.13 ±0.12	0.52 ±0.12
12/.0833	1.10 ±0.26	1.77 ±0.35	0.62 ±0.06

CONCLUSIONS

On the basis of data collected and analyzed the following conclusions were drawn:

1. Based on comparison of the values and their confidence interval it was equally beneficial to either optimize the degree of substitution or the addition rate of the cationic starch.

2. The Colloid Titration Ratio was not a good test for this research.

3. The use of regression analysis is an excellent tool for this type of analysis.

4. Cationic starch is a very good retention aid in a naturally buffered furnish which contains calcium carbonate.

5. The Dynamic Britt Jar was a good research tool for comparing retentions given by various polymer systems.

SUGGESTIONS FOR FURTHER WORK

1. Identical trials can be done but with more repetitions.

2. Handsheets can be made to see whether it is more

beneficial to optimize the degree of substitution rather than the addition to optimize strength.

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APPENDIX

APPENDIX I - COLLOID TITRATION DATA

#/TON -D.S.	ml. DDPM BLANK	ml. DDPM SAMPLE	ANIONIC DEMAND	AVERAGE DEMAND	ml.PVSAK BLANK	ml.PVSAK SAMPLE	CATIONIC DEMAND	AVERAGE DEMAND	CTR IONIC RATIO	AVERAGE CTR
BLANK	10.0	9.8	0.2		10.0	7.2	2.8		0.07	
BLANK	10.0	9.9	0.1	0.13	10.0	7.5	2.5	2.57	0.04	0.05
BLANK	9.0	8.9	0.1	0.06	10.6	8.2	2.4	0.21	0.04	0.02
4/.014	10.0	9.7	0.3		9.7	7.8	1.9		0.16	
4/.014	10.2	9.8	0.4	0.63	10.4	7.9	2.5	2.10	0.16	0.32
4/.014	11.1	9.9	1.2	0.49	10.7	8.8	1.9	0.35	0.63	0.27
4/.0307	10.0	9.7	0.3		9.8	8.5	1.3		0.23	
4/.0307	9.9	9.3	0.6	0.47	9.9	8.3	1.6	1.77	0.38	0.27
4/.0307	10.0	9.5	0.5	0.15	10.1	7.7	2.4	0.57	0.21	0.09
4/.0833	10.1	8.2	1.9		9.6	9.1	0.5		3.80	
4/.0833	10.3	8.3	2	1.50	10.1	9.7	0.4	1.03	5.00	3.02
4/.0833	10.2	9.6	0.6	0.78	10.2	8.0	2.2	1.01	0.27	2.46
8/.014	9.2	8.7	0.5		9.6	8.0	1.6		0.31	
8/.014	10.1	9.0	1.1	0.77	9.8	8.1	1.7	1.77	0.65	0.44
8/.014	9.8	9.1	0.7	0.31	9.9	7.9	2	0.21	0.35	0.19
8/.0307	10.2	9.4	0.8		10.0	8.2	1.8		0.44	
8/.0307	9.9	9.7	0.2	0.90	10.1	8.1	2	2.67	0.10	0.31
8/.0307	9.9	8.2	1.7	0.75	12.2	8.0	4.2	1.33	0.40	0.19
8/.0833	10.0	9.5	0.5		9.8	8.4	1.4		0.36	
8/.0833	10.1	9.3	0.8	0.90	10.0	8.5	1.5	1.57	0.53	0.56
8/.0833	10.2	8.8	1.4	0.46	10.2	8.4	1.8	0.21	0.78	0.21
12/.014	11.7	11.0	0.7		10.0	8.2	1.8		0.39	
12/.014	9.8	9.1	0.7	0.70	10.1	9.5	0.6	1.53	1.17	0.63
12/.014	11.2	10.5	0.7	0.00	10.2	8.0	2.2	0.83	0.32	0.47
12/.0307	10.0	9.0	1		10.0	8.0	2		0.50	
12/.0307	10.2	9.3	0.9	1.10	10.0	7.8	2.2	2.13	0.41	0.52
12/.0307	10.5	9.1	1.4	0.26	10.7	8.5	2.2	0.12	0.64	0.12
12/.0833	10.7	9.8	0.9		9.7	8.3	1.4		0.64	
12/.0833	10.7	9.7	1	1.10	9.8	8.0	1.8	1.77	0.56	0.62
12/.0833	9.9	8.5	1.4	0.26	10.0	7.9	2.1	0.35	0.67	0.06

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APPENDIX II - BRITT JAR VALUES

D.S.--#/TON	WET WEIGHT TARE WT.	WET WEIGHT GROSS WT.	WET WEIGHT NET WT.	DRY WEIGHT TARE WT.	DRY WEIGHT GROSS WT.	DRY WEIGHT NET WT.	WT. OF FIBER g/100ml
.0226--12	19.06	122.22	103.16	0.434	0.482	0.048	0.047
.0226--12	19.21	125.75	106.54	0.436	0.483	0.047	0.044
.0226--12	19.11	120.95	101.84	0.500	0.543	0.043	0.042
.0226--4	19.31	118.61	99.3	0.474	0.490	0.016	0.016
.0226--4	19.18	112.68	93.5	0.511	0.530	0.019	0.020
.0226--4	19.29	117.82	98.53	0.475	0.494	0.019	0.019
.0226--8	19.24	120.74	101.5	0.444	0.468	0.024	0.024
.0226--8	19.35	113.07	93.72	0.438	0.459	0.021	0.022
.0226--8	19.27	116.86	97.59	0.438	0.462	0.024	0.025
.0307--12	19.38	121.87	102.49				
.0307--12	19.19	112.4	93.21	0.440	0.456	0.016	0.017
.0307--12	19.02	108.84	89.82	0.477	0.492	0.015	0.017
.0307--4	19.17	122.72	103.55	0.358	0.380	0.022	0.021
.0307--4	19.27	112.85	93.58	0.351	0.373	0.022	0.024
.0307--4	19.22	117.41	98.19	0.501	0.522	0.021	0.021
.0307--8	19.37	120.93	101.56	0.352	0.373	0.021	0.021
.0307--8	19.05	112.5	93.45	0.440	0.459	0.019	0.020
.0307--8	19.28	117.74	98.46	0.352	0.373	0.021	0.021
.0833--12	19.13	118.77	99.64	0.465	0.489	0.024	0.024
.0833--12	19.24	119.27	100.03	0.498	0.528	0.03	0.030
.0833--12	19.21	118.8	99.59	0.506	0.529	0.023	0.023
.0833--4	19.27	113.99	94.72	0.441	0.454	0.013	0.014
.0833--4	19.23	111.29	92.06	0.479	0.493	0.014	0.015
.0833--4	19.46	123.49	104.03	0.343	0.360	0.017	0.016
.0833--8	19.32	112.4	93.08	0.442	0.467	0.025	0.027
.0833--8	19.46	116.45	96.99	0.439	0.463	0.024	0.025
.0833--8	19.17	108.03	88.86	0.200	0.223	0.023	0.026
BLANK	19.09	118.62	99.53	0.504	0.552	0.048	0.048
BLANK	19.07	112.83	93.76	0.516	0.562	0.046	0.049
BLANK	19.22	117.65	98.43	0.438	0.487	0.049	0.050

APPENDIX III - HARDNESS TITRATION VALUES

D.S.--#/TON	SAMPLE TITER ml EDTA	WATER TITER ml EDTA	REAL TITE ml EDTA	SAMPLE TITER ml.EDTA/ml filtrate	wt. of CaCO3 SAMPLE	HBOX ml EDTA	wt. of CaCO3 HBOX
.0226--12	24.0	2.4	21.6	0.864	0.086	43.7	0.165
.0226--12	23.6	2.4	21.2	0.848	0.085	43.7	0.165
.0226--12	23.9	2.4	21.5	0.86	0.086	43.7	0.165
.0226--4	23.1	2.4	20.7	0.828	0.083	43.7	0.165
.0226--4	23.8	2.4	21.4	0.856	0.086	43.7	0.165
.0226--4	24.0	2.4	21.6	0.864	0.086	43.7	0.165
.0226--8	23.1	2.4	20.7	0.828	0.083	43.7	0.165
.0226--8	23.2	2.4	20.8	0.832	0.083	43.7	0.165
.0226--8	23.0	2.4	20.6	0.824	0.082	43.7	0.165
.0307--12							0.165
.0307--12	23.0	2.4	20.6	0.824	0.082	43.7	0.165
.0307--12	23.0	2.4	20.6	0.824	0.082	43.7	0.165
.0307--4	22.1	2.4	19.7	0.788	0.079	43.7	0.165
.0307--4	22.3	2.4	19.9	0.796	0.080	43.7	0.165
.0307--4	22.9	2.4	20.5	0.82	0.082	43.7	0.165
.0307--8	20.5	2.4	18.1	0.724	0.072	43.7	0.165
.0307--8	20.3	2.4	17.9	0.716	0.072	43.7	0.165
.0307--8	20.0	2.4	17.6	0.704	0.070	43.7	0.165
.0833--12	24.5	2.4	22.1	0.884	0.088	43.7	0.165
.0833--12	24.6	2.4	22.2	0.888	0.089	43.7	0.165
.0833--12	24.0	2.4	21.6	0.864	0.086	43.7	0.165
.0833--4	24.8	2.4	22.4	0.896	0.090	43.7	0.165
.0833--4	25.0	2.4	22.6	0.904	0.090	43.7	0.165
.0833--4	24.4	2.4	22	0.88	0.088	43.7	0.165
.0833--8	24.0	2.4	21.6	0.864	0.086	43.7	0.165
.0833--8	23.0	2.4	20.6	0.824	0.082	43.7	0.165
.0833--8	24.0	2.4	21.6	0.864	0.086	43.7	0.165
BLANK	28.0	2.4	25.6	1.024	0.102	43.7	0.165
BLANK	28.5	2.4	26.1	1.044	0.104	43.7	0.165
BLANK	27.7	2.4	25.3	1.012	0.101	43.7	0.165

APPENDIX IV - RETENTION VALUES

D.S.--#/TON	% SAMPLE CONS.	% HBOX CONS.	% F.P. RETN.	AVG % F. P. RETN.	%CaCO3 RETN.	AVG %CaCO3 RETN.	% FINES RETN.	AVG % FINES RETN.
.0226--12	0.133	0.49	72.9%		47.9%		28.6%	
.0226--12	0.129	0.49	73.7%	73.5%	48.5%	48.1%	30.7%	30.2%
.0226--12	0.128	0.49	73.9%	0.4%	47.9%	0.3%	31.3%	1.2%
.0226--4	0.099	0.49	79.8%		49.7%		46.8%	
.0226--4	0.106	0.49	78.4%	78.9%	47.9%	48.5%	43.1%	44.5%
.0226--4	0.105	0.49	78.6%	0.6%	47.9%	0.8%	43.6%	1.6%
.0226--8	0.107	0.49	78.2%		49.7%		42.5%	
.0226--8	0.105	0.49	78.6%	78.3%	49.7%	49.9%	43.6%	42.9%
.0226--8	0.107	0.49	78.2%	0.2%	50.3%	0.3%	42.5%	0.5%
.0307--12	0.000							
.0307--12	0.099	0.49	79.8%	79.8%	50.3%	50.3%	46.8%	46.8%
.0307--12	0.099	0.49	79.8%	0.0%	50.3%	0.0%	46.8%	0.0%
.0307--4	0.100	0.49	79.6%		52.1%		46.3%	
.0307--4	0.104	0.49	78.8%	79.1%	51.5%	51.3%	44.1%	45.0%
.0307--4	0.103	0.49	79.0%	0.3%	50.3%	0.7%	44.7%	0.9%
.0307--8	0.093	0.49	81.0%		56.4%		50.1%	
.0307--8	0.092	0.49	81.2%	81.2%	56.4%	56.8%	50.6%	50.6%
.0307--8	0.091	0.49	81.4%	0.2%	57.6%	0.6%	51.1%	0.4%
.0833--12	0.112	0.49	77.1%		46.7%		39.8%	
.0833--12	0.119	0.49	75.7%	76.9%	46.1%	46.9%	36.1%	39.1%
.0833--12	0.109	0.49	77.8%	0.9%	47.9%	0.7%	41.5%	2.3%
.0833--4	0.104	0.49	78.8%		45.5%		44.1%	
.0833--4	0.105	0.49	78.6%	78.7%	45.5%	45.9%	43.6%	43.9%
.0833--4	0.104	0.49	78.8%	0.1%	46.7%	0.6%	44.1%	0.2%
.0833--8	0.113	0.49	76.9%		47.9%		39.3%	
.0833--8	0.107	0.49	78.2%	77.4%	50.3%	48.7%	42.5%	40.5%
.0833--8	0.112	0.49	77.1%	0.6%	47.9%	1.1%	39.8%	1.4%
BLANK	0.150	0.49	69.4%		38.2%		19.4%	
BLANK	0.153	0.49	68.8%	69.1%	37.0%	38.0%	17.8%	18.7%
BLANK	0.151	0.49	69.2%	0.2%	38.8%	0.7%	18.9%	0.7%